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Influence of the ice front velocity and of the composition of suspensions on thermal properties of bentonite materials prepared using freeze–casting process

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Abstract

The influence of (i) the ice front velocity in the freeze–casting process as well as the addition of two binders, (ii) the inorganic synthetic mineral laponite and (iii) the natural organic oligomer chitosan, on the microstructure and on thermal conductivity of bentonite materials prepared using the freeze–casting process were investigated by scanning electron and interferometric microscopies and the laser flash method. Prior to measurements, materials physico-chemical characteristics were determined using specific surface area, grain size and density measurements. Results show that the width of the strongly oriented pores obtained with the freeze–casting process is modified by the presence of binders, and that in turn, the thermal conductivity and anisotropy are also significantly modified.

Keywords: Phyllosilicates; Anisotropic materials; Laser flash technique; Porous ceramics

1. Introduction

In recent years, the freeze–casting process has become known as an environmental and cost effective shaping process for advanced materials with interconnecting pore channels. Even though several studies have been conducted on alumina samples,[1–3] very few papers have focused on clay-based materials and their properties. In addition, the study of properties of clay samples prepared by freeze–casting was rarely reported. Hostler et al.[4] studied the thermal conductivity of a montmorillonite clay sample and the influence of a binder (poly(vinyl alcohol)) on the microstructure and on the thermal properties. They showed that the polymer enhances the mechanical strength of the clay aerogel and decreases its thermal conductivity. Tang et al.[5] studied the thermal conductivity of compacted bentonites and determined the effective thermal conductivity of the sample. Accurate control of the microstructure is a key factor regarding thermal performances of insulating porous materials. Thermal properties of ceramics materials are important for applications involving heat transfer such as housing, substrates for electronics and high temperature processing. One of the key parameters which determine thermal performances is thermal conductivity. In clay-based materials, incorporating an amount of porosity can lead to final products with a thermal conductivity of the order of $0.1\ W\ m^{-1}\ K^{-1}$, suitable for thermal insulation applications. In addition to insulating behavior in a given direction, a potential application of anisotropic porous materials could be to transport heat in other directions. Such control of the microstructure can be achieved through the drying process since this step influences the pore size and shape distribution. The freeze–casting process can induce pore orientation resulting in an anisotropic porous material. Furthermore, this process does not disturb the

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arrangement of clay particles and does not introduce unexpected defects (cracks) in the material. It yields very anisotropic materials.

In this paper, we present the influence of (i) the ice front velocity and of (ii) the nature and presence of organic or inorganic binders on the microstructure of the final material in relation with the thermal conductivity on pore formation (mostly pore orientation and size), after freeze drying of natural clay mineral (bentonite) suspensions. The ice front solidification velocity was estimated through numerical modeling. Addition of a mineral binder with smaller grain size, which increases the number of grain boundaries per unit length of heat path, decreases the thermal conductivity of the solid phase. Finally, the anisotropic ratio of thermal conductivity is determined for all prepared materials.

2. Materials and methods

2.1. Materials

Bentonite (Optigel CK, $(Al_{3,2}Mg_{0,8})(Si_8)O_{20}(OH)_4Na_{0,8}(H_2O)_{0.8}$) and laponite ($Si_8(Mg_{5,5}Li_{0,3})O_{20}(OH)_4]Na_{0,7}$) powders were purchased from Rockwood Additives (Widnes, United Kingdom). Powder specific surface area was determined with the Brunauer–Emmet–Teller (BET) method using adsorption of nitrogen at 77 K (Tristar Micromeritics, USA). Grain size was estimated using a laser size analyzer (Nanosizer, Malvern Instrument, UK) and the true density was measured with a helium pycnometer (Micromeritics AccuPyc 1330, USA). Powder characteristics are summarized in Table 1.

Chitosan (medium molecular weight), a derivative of chitin, a natural polymer found in shellfish, was purchased from Sigma Aldrich, USA.

2.2. Preparation of suspensions

Clay mineral aqueous suspensions were prepared by dispersing 6 g of clay powder in 100 g of deionized water with 7 wt% sodium hexametaphosphate (SHMP, $Na_6P_6O_{18}$). After 30 min. stirring, an organic binder (a 0.02 g mL^{-1} chitosan solution obtained by dissolving 2 g of chitosan in 100 mL of 1 vol.% hydrochloric acid) or an inorganic binder (laponite, a nano-sized synthetic phyllosilicate powder) was slowly added. The binding agent concentration was kept constant at 0.5 wt% in both cases. The mixtures were then stirred continuously for 4 h.

2.3. Process

The mold used for freeze–casting consists of adjustable aluminum sides on a removable poly-(tetrafluoroethylene, PTFE) bottom, to ensure an oriented temperature gradient during the freezing step. In order to vary the ice front velocity, the mold was cooled to different temperatures (249 K, 208 K and 77 K) before the casting of the suspension. Initially at room temperature, the suspension was then introduced in the mold and cooled at one of the temperatures indicated above. Subsequently, the sample was placed in the vacuum chamber (1.2 Pa) of a freeze-drier (BETA 2-8 LDPlus, CHRIST, Germany) for 24 h. Furthermore, air-dried bentonite samples obtained from suspensions with the same concentration were prepared as references for microstructure and conductivity measurements. These samples were simply cast in 10 cm diameter × 3 cm height mold and let dry at room temperature for approximately one week. Macroscopically homogeneous samples were obtained. For the thermal conductivity study, three samples were also prepared by uniaxialy pressing at 10 MPa, 30 MPa and 300 MPa. All the samples were consolidated at 800 °C. At this temperature, phyllosilicates already underwent a deshydroxylation step inducing a structural modification but it is sufficiently low to prevent the formation of mullite, which is more thermally conducting than bentonite. Since one aim of this work is to give some insight into clay-based materials heat transport through elongated pores, this consolidating temperature allowed to preserve as much porosity as possible, to optimize thermal conductivity properties.

Table 1
Bentonite and laponite powders properties.

	Bentonite	Laponite
Specific surface area ($m^2\ g^{-1}$)	43	364
Average grain size (d_{50}, nm)	450	10–20
Density ($g\ cm^{-3}$)	2.5	2.3

2.4. Microstructure characterization

Microstructures of the freeze-dried samples were observed using scanning electron microscopy (Cambridge Scientific Instrument, UK). The microscope was used with an accelerating voltage of 15 kV. Interferometric microscopy (Fogale Nanotech, France) has been employed to evaluate overall the roughness of the sample and the surface morphology.

2.5. Thermal conductivity measurement

Laser flash method was used to determine, via the thermal diffusivity, the effective thermal conductivity of the samples. The flash source is a neodymium-doped phosphate glass laser operating at 1.053 μm. This laser which delivers a standard pulse of 30 J in 450 μs was used to heat up the front face of the cylindrical sample. The absorbed heat diffuses throughout the sample and a liquid-nitrogen-cooled infra-red detector (Hg–Cd–Te) was used to monitor the evolution of the back face temperature. Samples were coated with a thin graphite layer in order to avoid the transmission of the laser radiation through the thickness of the material and to improve the laser beam absorption and the emitted signal of the back face. After receiving the laser pulse, the wavelength of the emitted radiation from the coated surfaces is in the order of 10 μm, corresponding to the sample temperature (near 300 K). For such wavelengths, we can assume that the pore walls are opaque and radiative heat transfer from front and rear surfaces do not have to be considered. This is confirmed by the signal which does not exhibit a significant immediate increase of the temperature back face when sending the laser pulse as described in literature.[6,7] Typical dimensions of the disk samples were 2 mm in thickness and 10 mm in